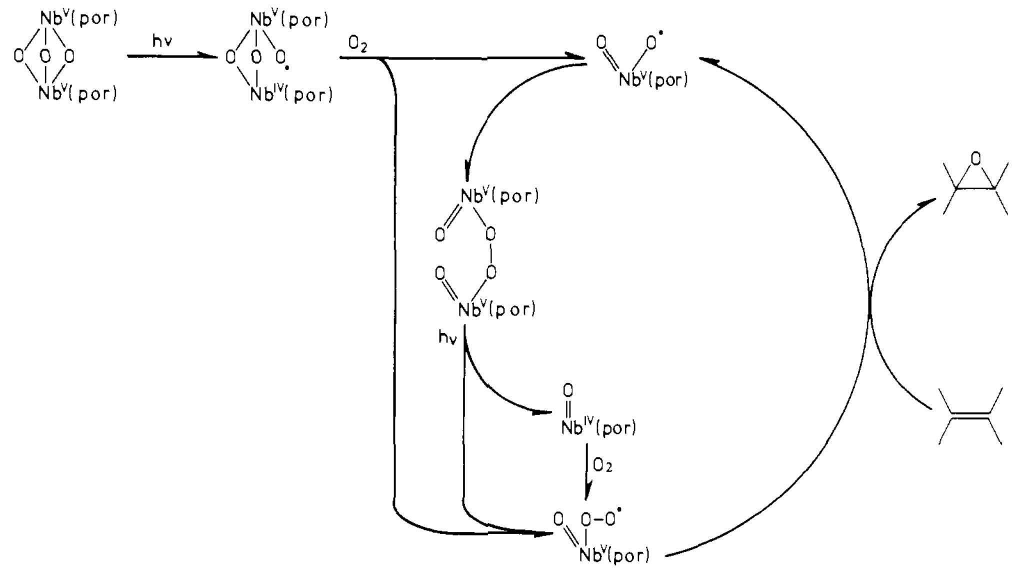
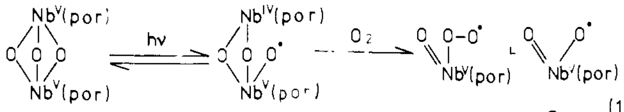
Scheme I

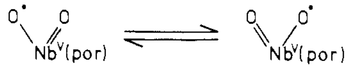


which is ESR silent. These observations are consistent with the photochemical homolysis of the Nb–O bond and the subsequent attack by dioxygen as shown by eq 1. Although both niobium



1 **2** **3** (1)

species **2** and **3** are considered to be paramagnetic, **3** seems to become ESR silent because it may have a short relaxation time due to the exchange process given by eq 2. As a consequence,



(2)

3 is responsible for oxidation of the heterocyclic bases, and the recombination of **2** and **3**, which takes place after interruption of aerobic irradiation, is disturbed due to loss of the latter; the lifetime of **2** becomes larger as shown in Figure 2.

The ESR signal was immediately quenched when olefins were added to a benzene solution of **1** under the aerobic irradiation conditions, indicating that the reaction of olefins with **2** takes place. The products were analyzed by GLC as summarized in Table I. Cyclohexene, 2,3-dimethyl-2-butene, and 1-hexene afforded exclusively the corresponding epoxides, and any products oxidized at the allyl site were not detected by GLC analysis after the reaction periods shown in Table I. Since the product yields were well over quantitative after certain reaction periods studied here, the reaction must proceed catalytically. The substrate with a terminal double bond, 1-hexene, shows lower reactivity relative to the others. This seems to be attributed to the lower oxygen affinity of terminal olefins. 2,3-Dimethyl-2-butene was transformed into the corresponding epoxide in a good yield, while 2,3-dimethyl-2-hydroperoxybutane was recovered without any transformation under the identical experimental conditions. This strongly indicates that singlet oxygen, which produces allylic oxidation products, is not involved during the present oxygenation reaction. The epoxidation of cyclohexene was somewhat depressed upon addition of pyridine to the reaction system, while addition of pyridine resulted in enhancement of the ESR signal originated from **2** under the comparable conditions without the substrate. Thus, the ESR silent species (**3**) presumably participates in the catalytic cycle, and its inactivation by the reaction with pyridine (vide supra) disturbs regeneration of the catalytically active species. The catalytic cycle is plausibly illustrated by Scheme I in the light of the present observations. The advantageous aspects of the present catalyst system are as follows: (i) The atmospheric oxygen molecule can be utilized as a single oxygen atom source for selective epoxidation; (ii) molecular oxygen can be activated without any additional reductants. The preparation of niobium catalysts with other organic ligands is under current investigation.

Disilylation of Acetylenes with Si–Mn Reagent

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Received May 22, 1985

Previously reported reaction of Si–Mg, Si–Al, or Si–Zn reagents with an acetylenic linkage affords simple and general access to the cis-addition products of the component atoms.[1] The regiochemistry is dependent on the transition-metal catalysts employed and the reaction is useful in synthetic work.[2] In further extension of this technique, we have examined the reaction of Si–Mn reagent with acetylenes to observe rather unexpected formation of disilylated products.[3]

Typical experimental procedure is as follows. Methyllithium (1.4 M, 3.2 mL, 4.5 mmol) was added to a solution of hexamethyldisilane (0.93 mL, 4.5 mmol) in THF (8 mL)–HMPA (2 mL) at 0 °C. After the mixture was stirred for 15 min, methylmagnesium iodide (1.5 M, 3.0 mL, 4.5 mmol) was added to the resulting solution of (trimethylsilyl)lithium. The mixture was stirred for another 15 min and anhydrous manganese(II) chloride (0.19 g, 1.5 mmol) was added in one portion.[4,5] Then a solution

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(1) Hayami, H.; Sato, M.; Kanemoto, S.; Morizawa, Y.; Oshima, K.; Nozaki, H. *J. Am. Chem. Soc.* **1983**, *105*, 4491.

(2) Morizawa, Y.; Oda, H.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1984**, *25*, 1163. Okuda, Y.; Morizawa, Y.; Oshima, K.; Nozaki, H. *Ibid.* **1984**, *25*, 2483.

(3) Palladium(0)-catalyzed double silylation of acetylenes with disilanes of special substituents such as hydro, fluoro, and methoxy group gave the corresponding silyl olefins in good yield. In contrast, hexamethyldisilane gave very poor yields of double-silylated products. Watanabe, H.; Kobayashi, M.; Saito, M.; Nagai, Y. *J. Organomet. Chem.* **1981**, *216*, 149 and references cited therein.

(4) The addition of 3 equiv of BuLi to $MnCl_2$ is known to give Bu_3MnLi (Normant, J.-F.; Cahiez, G. "Modern Synthetic Methods 1983"; Salle Verlag: Frankfurt/M, 1983; pp 173–216. Kauffmann, T.; Bisling, M. *Tetrahedron Lett.* **1984**, *25*, 293). We are tempted to assume that the active reagent in our new method could be $(Me_3Si)_3MnMgMe$ derived from 3 equiv of $Me_3SiMgMe$ and $MnCl_2$. The addition of PhCHO to the reagent provided only phenyl(trimethylsilyl)carbinol and no trace of 1-phenylethanol.

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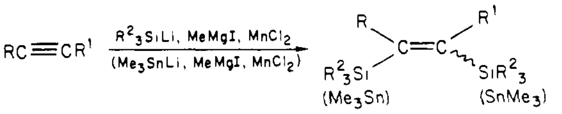
Table I. Disilylation or Distannylation of Acetylenes with Si–Mn or Sn–Mn Reagent



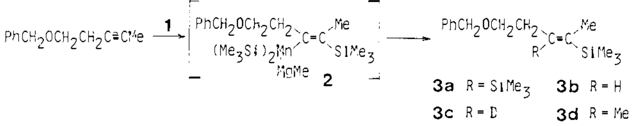
acetylene $RC{\equiv}CR^1$	reagent R^2_3SiLi	product yield, %	 Z/E
$HC{\equiv}CSiMe_3$	Me_3SiLi	72	
$C_4H_9C{\equiv}CH$	Me_3SiLi	66	33/67
$PhC{\equiv}CH$	Me_3SiLi	65	50/50
$C_4H_9C{\equiv}CSiMe_3$	Me_3SiLi	80	
$PhCH_2OCH_2CH_2C{\equiv}CH$	$PhMe_2SiLi^a$	51	42/58
$PhCH_2OCH_2CH_2C{\equiv}CD$	$PhMe_2SiLi$	55	$42/58^b$
$PhCH_2OCH_2CH_2C{\equiv}CSiMe_3$	Me_3SiLi	59	
$THPOCH_2CH_2C{\equiv}CH$	Me_3SiLi	63	65/35
$THPOCH_2CH_2C{\equiv}CH$	$PhMe_2SiLi$	70	65/35
$THPOCH_2CH_2C{\equiv}CSiMe_3$	Me_3SiLi	83	
$HOCH_2CH_2C{\equiv}CSiMe_3$	Me_3SiLi^c	58	
$C_{10}H_{21}C{\equiv}CH$	Me_3SnLi^d	56	100/0
$C_{10}H_{21}C{\equiv}CD$	Me_3SnLi	55	$100/0^b$
$THPOCH_2CH_2C{\equiv}CH$	Me_3SnLi	54	100/0
$THPOCH_2CH_2C{\equiv}CH$	Bu_3SnLi^d	48	90/10
$PhCH_2OCH_2CH_2C{\equiv}CH$	Me_3SnLi	52	90/10

[a] See ref 6. [b] Deuterium remained completely, thus reagents do not cause the acetylenic proton–metal exchange. [c] Three millimoles of manganese reagent and 1 mmol of substrate were employed. [d] See ref 7.

of tetrahydropyranyl ether of 4-(trimethylsilyl)-3-butyn-1-ol (0.23 g, 1.0 mmol) in THF (3 mL) was added and the resulting mixture was stirred for 3 h at 0 °C. The mixture was diluted with ether and poured into saturated NH_4Cl. Purification by preparative TLC on silica gel gave tetrahydropyranyl ether of 3,4,4-tris(trimethylsilyl)-3-buten-1-ol (0.31 g) in 83% yield as a colorless oil: bp 150 °C (1.0 torr, bath temperature); IR (neat) 1440, 1350, 1260, 1250, 1200, 1140, 1120, 1030, 840 cm^{-1}; NMR ($CDCl_3$) δ 0.19 (s, 9 H), 0.22 (s, 9 H), 0.23 (s, 9 H), 1.5–1.9 (m, 6 H), 2.89 (t, J = 8 Hz, 2 H), 3.36 (dt, J = 8, 10 Hz, 1 H), 3.5–3.6 (m, 1 H), 3.66 (dt, J = 8, 10 Hz, 1 H), 3.8–3.9 (m, 1 H), 4.61 (t, J = 3 Hz, 1 H); MS, m/z 372 (M^+, 1), 270 (64), 197 (43), 155 (48), 85 (100), 73 (99). Found: C, 58.02; H, 11.06%. Calcd for $C_{18}H_{40}O_2Si_3$: C, 58.00; H, 10.82%.

For other examples see Table I. The reaction proceeded smoothly with silylacetylenes as well as terminal acetylenes. Terminal acetylenes gave mixtures of E and Z isomers of disilylated products. MeMgI is essential for the formation of disilylated products, although its role is not clear. Without MeMgI, monosilylated products were obtained predominantly after aqueous workup. For instance, treatment of 4-(benzyloxy)-1-butyne with $3Me_3SiLi{-}MnCl_2$ gave a mixture of 4-(benzyloxy)-2-(trimethylsilyl)-1-butene, 4-(benzyloxy)-1-(trimethylsilyl)-1-butene, and disilylated product in 1:1:1 ratio (65% combined yield). The reaction has been extended to distannylation of acetylenes. See Table I.

Treatment of 5-(benzyloxy)-2-pentyne with the reagent $(Me_3Si)_3MnMgMe$ (**1**) at 0 °C for 20 min and 25 °C for 3 h gave 2,3-bis(trimethylsilyl)-2-alkene **3a** in 78% yield. Meanwhile, the addition of H_2O (or D_2O, MeI) to the reaction mixture after stirring at 0 °C for 20 min without warming up to room temperature gave monosilylated product **3b** (71%) (or **3c** (71%), **3d** (70%)) along with the disilylated product **3a** (13–20%).[8] Thus, the formation of disilylated product may be explained as follows: (1) Addition of the reagent **1** to triple bond in cis fashion[9] giving silylated alkenylmanganese **2** and (2) reductive elimination of manganese affording disilylated olefin.



It is worth noting that the reaction can be successfully applied to the synthesis of highly strained tetrakis(trimethylsilyl)ethene which is not readily available by known methods.[10]

$$\mathrm{Me_3SiC{\equiv}CSiMe_3} \xrightarrow[\text{THF/HMPA, 76\%}]{\mathrm{Me_3SiLi,\ MeMgI,\ MnCl_2}} \mathrm{(Me_3Si)_2C{=}C(SiMe_3)_2}$$

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[5] A solution of Li_2MnCl_4 in THF could be used instead of $MnCl_2$.

[6] A stock solution in THF was used. Gilman, H.; Lichtemwalter, G. D. *J. Am. Chem. Soc.* **1958**, *80*, 607.

(7) Prepared from $SnCl_2$ and 3 equiv of alkyllithium. Hibino, J.; Matsubara, S.; Morizawa, Y.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1984**, *25*, 2151.

(8) In the case of terminal acetylenes and silylacetylenes in Table I, the intermediary alkenylmanganese could not be trapped by the electrophiles such as D_2O and MeI.

(9) The cis addition of Si–Mn component was confirmed as follows. Monosilylated alkene, 5-(benzyloxy)-2-(dimethylphenylsilyl)-2-pentene was prepared from $(PhMe_2Si)_3MnMgMe$ and 5-(benzyloxy)-2-pentyne according to the generation of **3b**. Protodesilylation with n-Bu_4NF (Oda, H.; Sato, M.; Morizawa, Y.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1983**, *24*, 2877) gave 5-(benzyloxy)-2-pentene. The examination of the ^1H NMR spectra proved that the olefin had Z configuration (>95%, J = 11 Hz).

(10) Sakurai, H.; Nakadaira, Y.; Kira, M.; Tobita, H. *Tetrahedron Lett.* **1980**, *21*, 3077. Chung, C.; Lagow, R. J. *J. Chem. Soc., Chem. Commun.* **1972**, 1078.

Palladium-Catalyzed Annelation onto *N*,*N*-Dialkylanilines by Tetrahydrofuran. Stereospecific Formation of Heterotricyclic Compounds via Cation Radical Intermediates

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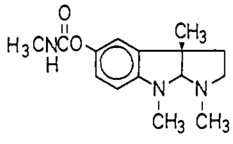
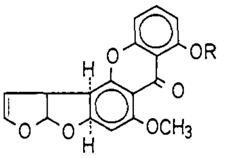
Received April 9, 1985

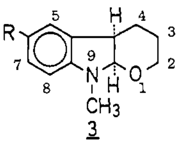
The natural compounds with cis-[2,3-*b*]-fused N,N- or O,O-diheterobicyclic structures, such as physostigmin (**1**) and strigmatocystins (**2**), are interesting due to their pharmacology[2] and synthetically challenging structures. We now report a facile method to obtain a new class of heterotricyclic compounds **3** containing cis-[2,3-*b*]-fused N,O-diheterobicyclic structure by palladium(II)-assisted annelation onto *N*,*N*-dialkylanilines by tetrahydrofuran. The reactions may be explained in terms of a formation of *N*,*N*-dialkylaniline cation radicals.



1



2 R ;H,CH3



3

R ;H,CH3,OCH3

In arene oxidation by metal salts, a recent monograph[3] noted that free cation radicals are formed with hard metal ions such

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(1) Physical Institute, College of Liberal Arts.

(2) (a) Glasby, J. S. "Encyclopedia of the Alkaloids"; Plenum Press: New York, 1975; Vols. I, II. (b) Shibata, S. "Bioactive Natural Products" (in Japanese); Ishiyaku Press: Tokyo, 1979; pp 397–402. (c) Natori, S. *Yakugaku Zasshi* **1983**, *103*, 1109. Udagawa, S.; Muroi, T.; Sekita, S.; Yoshihira, K.; Natori, S.; Ueda, M.; *Can. J. Microbiol.* **1979**, *25*, 170. Sekita, S.; Yoshihira, K.; Natori, S.; Udagawa, S.; Muroi, T.; Sugiyama, Y.; Kurata, H.; Umeda, M.; *Ibid.* **1981**, *27*, 766.

(3) Shelden, R. A.; Kochi, J. K. "Metal-Catalyzed Oxidation of Organic Compounds"; Academic Press: New York, 1981; pp 130–133.

0002-7863/85/1507-6417$01.50/0